Spin gap behavior in $Cu_2Sc_2Ge_4O_{13}$ by ^{45}Sc nuclear magnetic resonance

C. S. Lue[1,*], C. N. Kuo[1], T. H. Su[1], and G. J. Redhammer[2,†]
[1]*Department of Physics, National Cheng-Kung University, Tainan 701, Taiwan*
[2]*Department of Material Science, Division of Mineralogy, University of Salzburg, Hellbrunnerstr. 34, Salzburg A-5020, Austria*
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We report the results of a ^{45}Sc nuclear magnetic resonance (NMR) study on the quasi-one-dimensional compound $Cu_2Sc_2Ge_4O_{13}$ at temperatures between 4 and 300 K. This material has been a subject of current interest due to indications of spin gap behavior. The temperature-dependent NMR shift exhibits a character of low-dimensional magnetism with a negative broad maximum at $T_{max} \simeq 170$ K. Below T_{max}, the NMR shifts and spin lattice relaxation rates clearly indicate activated responses, confirming the existence of a spin gap in $Cu_2Sc_2Ge_4O_{13}$. The experimental NMR data can be well fitted to the spin dimer model, yielding a spin gap value of about 275 K which is close to the 25 meV peak found in the inelastic neutron measurement. A detailed analysis further points out that the nearly isolated dimer picture is proper for the understanding of spin gap nature in $Cu_2Sc_2Ge_4O_{13}$.

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I. INTRODUCTION

The physics of low-dimensional magnetic systems continues to attract attention because of the association with peculiar quantum effects.[1] Prominent examples like the spin-Peierls transition and the spin ladder compounds have been characterized by ground states of the spin singlet with a finite spin gap.[2, 3] For a quasi-one-dimensional chain with half-integer spin ($S = 1/2$), the gap can be opened via either frustration due to next nearest neighbor antiferromagnetic exchange or dimerization due to an alternating coupling to nearest neighbors along the chain.[4, 5] Several $S = 1/2$ chain systems such as $(VO)_2P_2O_7$, $BaCu_2V_2O_8$, and $PbCu_2(PO_4)_2$ have been reported to possess spin gaps and their characteristics have been interpreted in accordance with these scenarios.[6, 7, 8]

$Cu_2Sc_2Ge_4O_{13}$, which crystallizes in a monoclinic structure with the space group $P2_1/m$, was recently synthesized by one of the present authors (G.J.R.).[9] A schematic picture of the crystal structure is illustrated in Fig. 1. Taking into account the known oxidation states of O^{2-} and Ge^{4+}, the remaining valences are nonmagnetic Sc^{3+} and Cu^{2+} ($S = 1/2$). The spin chain in $Cu_2Sc_2Ge_4O_{13}$ can be described as an arrangement of spin dimers oriented along the crystallographic b-axis, separated by GeO_4 tetrahedra and crankshaft-like chains of ScO_6 octahedra (Fig. 1). Each dimer consists of two Cu^{2+} ions in a Cu_2O_2 plaquette and weak interdimer interactions could be possible to induce a quantum phase transition from a gapless state into a gapped state for $Cu_2Sc_2Ge_4O_{13}$.

The bulk magnetic susceptibility of $Cu_2Sc_2Ge_4O_{13}$ exhibits a broad maximum at around 170 K and decreases rapidly at low temperatures, indicative of spin gap behavior for this material.[10] Also the magnetization data have been fitted well to the dimer chain model, yielding a spin gap of 290 K (25 meV). Furthermore, the result of heat capacity has confirmed no magnetic ordering above 2 K.[10] Recently, Masuda *et al.* have performed a neutron inelastic-scattering experiment on $Cu_2Sc_2Ge_4O_{13}$ and found a narrow-band excitation of about 25 meV, which is quite consistent with the value extracted from the susceptibility.[10] They thus attributed the observation to the spin-gap excitation and proposed $Cu_2Sc_2Ge_4O_{13}$ as a new spin-gapped dimer material.

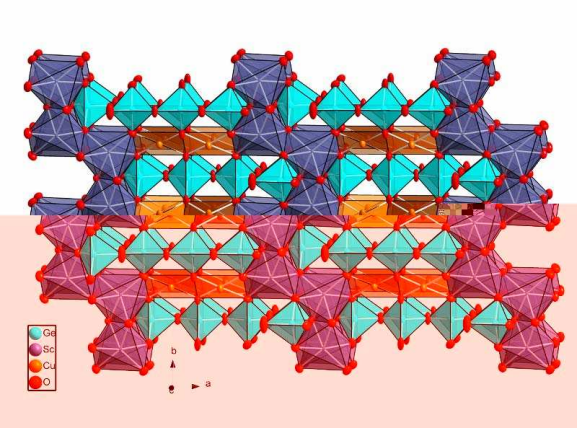

FIG. 1: Crystal structure for $Cu_2Sc_2Ge_4O_{13}$.

In order to further identify the existence of a spin gap in $Cu_2Sc_2Ge_4O_{13}$, we carried out a detailed ^{45}Sc nuclear magnetic resonance (NMR) study invoking NMR shifts and spin-lattice relaxation rates on this compound. The NMR shift provides a local measurement of the susceptibility which is less sensitive to the presence of impurities

*Email: cslue@mail.ncku.edu.tw
†Email: guenther.redhammer@aon.at

and other phases. The spin-lattice relaxation rate is a sensitive probe for the low-energy spin excitations, yielding direct evidence for the presence of an energy gap. Regarding the title compound $Cu_2Sc_2Ge_4O_{13}$, a transfer of magnetic d-spin from the Cu^{2+} onto Sc^{3+} $4s$ orbital allows us to probe the Cu^{2+} spin dynamics and determine the spin gap through the transfer hyperfine interaction. The experimental NMR results clearly reveal spin gap behavior in this material. Data analysis using the isolated dimer model is found to give good agreement with the observations. Interestingly, the deduced spin gap value of 275 K is close to the 25 meV peak revealed by the inelastic neutron experiment,[10] indicating the same energy excitation detected by both measurements.

II. EXPERIMENTS AND DISCUSSION

A polycrystalline $Cu_2Sc_2Ge_4O_{13}$ sample was synthesized by a ceramic sintering solid-state reaction technique.[9] A mixture of CuO, Sc_2O_3 and GeO_2, weighted in a predetermined molar ration of $Cu_2Sc_2Ge_4O_{13}$, was carefully ground under alcohol, pressed into pellets, put into an open platinum crucible, and fired under ambient pressure and ambient oxygen fugacity in a temperature range between 900 °C and 1100 °C. After each of six heating cycle, the sample was reground, pressed, and reheated. In initial stages the product consisted of a mixture of the title compound and $CuGeO_3$. The amount of $CuGeO_3$ reduced successively as increasing synthesis temperature and heating time. In a final synthesis cycle, the sample was fired at 1150 °C and a light blue product was thus obtained. A room-temperature x-ray diffraction confirmed the single phase for $Cu_2Sc_2Ge_4O_{13}$ with the lattice parameters a =12.336(2) $\mathring{A}$, b =8.7034(9) $\mathring{A}$, c =4.8883(8) $\mathring{A}$, and β =95.74(2).

NMR experiments were performed using a Varian 300 spectrometer, with a constant field of 7.05 T. A home-built probe was employed for the low-temperature measurements.[11] The powder specimen was put in a plastic vial that showed no observable ^{45}Sc NMR signal. The NMR spectrum was obtained from spin echo fast Fourier transforms using a standard $\pi/2-\tau-\pi$ sequence. Within the $P2_1/m$ space group for $Cu_2Sc_2Ge_4O_{13}$, scandium atoms occupy one crystallographic site having octahedral oxygen coordination, yielding an one-site ^{45}Sc NMR powder pattern, as demonstrated in the inset of Fig. 2. Here the observed NMR line shape is manifested by the anisotropic Knight shift as well as the quadrupole effects. However, no visible quadrupole edges have been detected with our static NMR probe, suggesting that the value of quadrupole frequency ν_Q is essentially small. Such a result indicates that the Sc atoms are located in a symmetric environment, probably at the center of the ScO_6 octahedron. It is of great importance to note that the line shape of the spectrum remains unchanged with temperature. This phenomenon confirms the nonmagnetic ground state for $Cu_2Sc_2Ge_4O_{13}$ and no structural changes above 4 K.

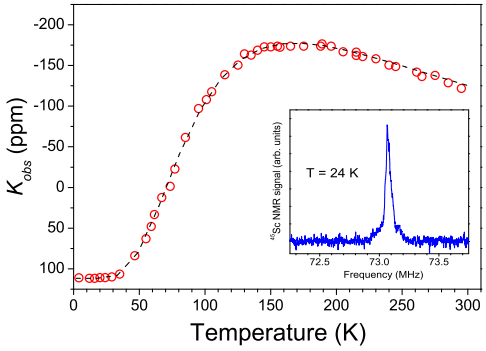

FIG. 2: Temperature dependence of the observed ^{45}Sc NMR shift in $Cu_2Sc_2Ge_4O_{13}$. Note that K_{obs} is shown by the negative direction. Dashed curve: fit to the dimer model plus a constant term. Inset: ^{45}Sc NMR spectrum for $Cu_2Sc_2Ge_4O_{13}$ measured at 24 K.

In Fig. 2, we displayed the observed temperature-dependent NMR shift (K_{obs}) for the Sc site. The shift was taken at the peak position of the resonance line referred to the ^{45}Sc resonance frequency of aqueous $ScCl_3$. Here K_{obs} has different sign from that of the susceptibility since the transfer hyperfine field arising from $3d$ electrons of Cu^{2+} ions is negative. In spite of the sign difference of K_{obs}, the whole temperature variation is quite consistent with the bulk susceptibility data, with a broad maximum at around $T_{max} \simeq 170$ K and a rapid decrease as lowering temperature.[10] In general, K_{obs} can be decomposed into $K_{obs} = K_o + K_{spin}(T)$. The first term $K_o = 112$ ppm, mainly arising from the orbital shift, is independence of temperature. On the other hand, the spin shift K_{spin}, which reflects the Cu^{2+} spin behavior through the transfer hyperfine interaction, is a function of temperature.

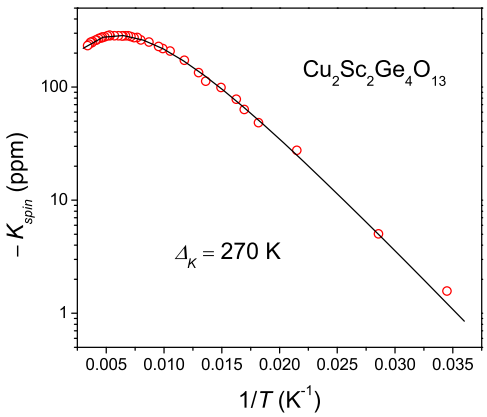

FIG. 3: Plot of K_{spin} against $1/T$ for $Cu_2Sc_2Ge_4O_{13}$. Solid curve: fit to the function described by the dimer model with Δ_K of 270 K.

As mentioned above, the spin chain configuration of

spin dimers could be responsible for the magnetic behavior of $Cu_2Sc_2Ge_4O_{13}$. Accordingly, the temperature dependence of the spin shift will obey the relation $K_{spin} \propto 1/T(3 + e^{\Delta_K/T})$.[12] Here Δ_K is the gap energy determined from the NMR shift based on the dimer model. As demonstrated in Fig. 3, K_{spin} can be fitted well in a fairly wide temperature range to this relation (solid curve in Fig. 3). It is also found that K_{spin} vanishes to almost zero at low temperatures, indicative of the gap in the spin excitation spectrum. With this fit, we extracted $\Delta_K = 270\pm20$ K, consistent with 290 K obtained from the susceptibility measurement.[10]

The spin shift here is related to the magnetic susceptibility χ by the expression

$$K_{spin}(T) = \frac{H_{hf}^{tr}}{N_A \mu_B}\chi(T), \qquad (1)$$

where H_{hf}^{tr} is the transfer hyperfine field due to an intermixing of Sc and Cu spin states, N_A is the Avogadro's constant, and μ_B is the Bohr magneton. The Clogston-Jaccarino plot[13] which shows the observed shift against magnetic susceptibility (deduced from the data of Ref. 10) is given in Fig. 4. The linear behavior indicates a unique hyperfine field over the entire temperature range we investigated. The slope yields a small value of $H_{hf}^{tr} = -0.66\pm0.04$ kOe.

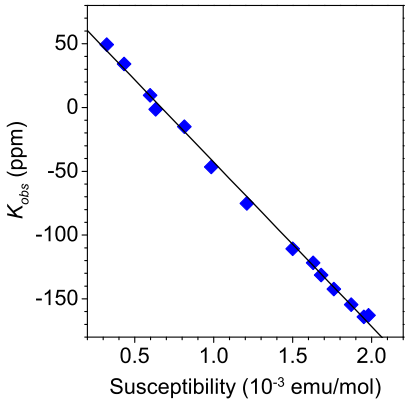

FIG. 4: Variation of K_{obs} versus χ (deduced from Ref. 10)

To gain more insight into the spin gap characteristics of $Cu_2Sc_2Ge_4O_{13}$, we performed spin-lattice relaxation rate $(1/T_1)$ measurements, being sensitive to the low-energy magnetic excitations. It thus provides direct information about the low-energy spin dynamics and the presence of a spin gap. Here the T_1 measurement was carried out using the saturation recovery method. The saturation rf comb with 30 short 2 μs pulses was employed. We recorded the recovery of the signal strength by integrating the ^{45}Sc spin echo signal. For the central transition with $I = 7/2$, the recovery of the nuclear magnetization follows[14]

$$\frac{M(t)}{M(0)} = 0.012e^{-\frac{t}{T_1}} + 0.068e^{-\frac{6t}{T_1}} + 0.206e^{-\frac{15t}{T_1}} + 0.714e^{-\frac{28t}{T_1}}. \qquad (2)$$

Here $M(t)$ is the magnetization at the recovery time t and $M(0)$ is the initial magnetization. The T_1 value was thus obtained by fitting to this multi-exponential function. To provide accurate values, each T_1 has been measured several times and the averaged T_1 for the corresponding temperature is shown in the inset of Fig. 5. It is apparent that $1/T_1$ exhibits activated behavior at low temperatures. Based on the dimerized scenario, the spin-lattice relaxation rate should be fitted to the form $1/T_1 \propto 1/(3 + e^{\Delta_R/T})$ by analogy to the treatment of NMR shift.[12] The fitting result, drawn in Fig. 5 as a solid curve, is quite satisfactory and yields an energy gap $\Delta_R = 275\pm25$ K. Remarkably, this excitation energy is almost identical with the 25 meV (290 K) peak obtained in the inelastic neutron experiment,[10] pointing to the same energy excitation probed by both measurements.

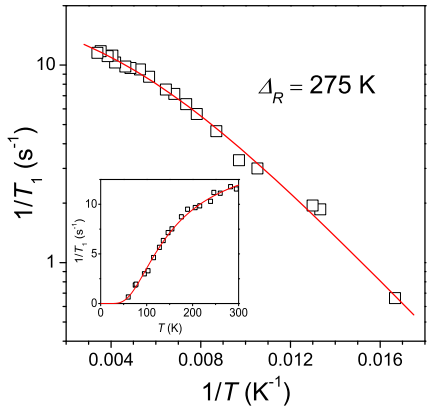

FIG. 5: Inverted temperature dependence of $1/T_1$ for $Cu_2Sc_2Ge_4O_{13}$. The solid curve is the fitted function based on the dimer model. Inset shows the temperature variation of $1/T_1$.

Our NMR investigation thus provides clear evidence for the existence of spin gap in $Cu_2Sc_2Ge_4O_{13}$. The extracted Δ_K was found to be close to Δ_R. As a matter of fact, the ratio of $\Delta_R/\Delta_K \simeq 1$ is commonly seen in the dimerized systems.[15, 16] Within the isolated dimer limit, T_{max}, the temperature at which magnetic susceptibility or NMR shift display a maximum, will appear at around $0.63\Delta_R$.[17] For the present case of $Cu_2Sc_2Ge_4O_{13}$, the determined $\Delta_R = 275$ K results in $T_{max} = 173$ K, in excellent agreement with the observed $T_{max} \simeq 170$ K. In this regard, it seems reasonable to characterize $Cu_2Sc_2Ge_4O_{13}$ as a nearly isolated dimer chain compound.

At this moment, we did not attempt to fit the temperature dependence of spin shift and $1/T_1$ to other models such as the alternating chain model. In fact, our previous analyses of NMR data for $BaCu_2V_2O_8$ indicated that both alternating chain and dimer chain models are suitable for the understanding of the spin gap nature.[18] However, a convincing result can be established unambiguously from the comparison of static and dynamic excitations. Within the dimer picture, the excitation is

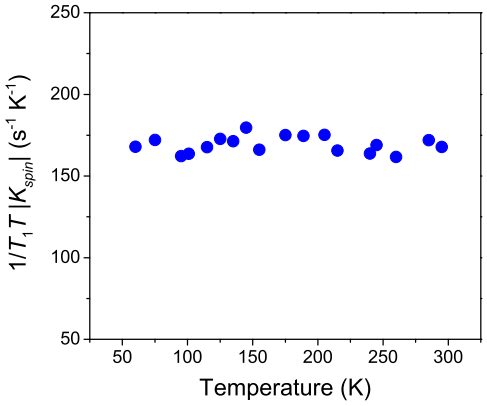

FIG. 6: Temperature variation of $(T_1T)^{-1}/\mid K_{spin} \mid$.

predominant by a simple singlet-triplet process.[19] As a result, the static susceptibility probed by K_{spin} and the local dissipative susceptibility probed by $(T_1T)^{-1}$ are nearly identical. On the other hand, for weakly coupled Heisenberg spin chains, both triplet and singlet-triplet mechanisms contribute to the relaxation rate.[20] In this case, the temperature dependence of $(T_1T)^{-1}$ becomes more prominent than that of K_{spin} as $T < \Delta_K$, leading to a larger spin gap deduced by $1/T_1$.[21, 22, 23, 24] Such a phenomenon has been observed in the S =1 Haldane gap compound Y_2BaNiO_5 and the S =1/2 spin chain $BaCu_2V_2O_8$.[25, 26] To provide a reliable spin gap description for $Cu_2Sc_2Ge_4O_{13}$, we thus examine the temperature dependence of $(T_1T)^{-1}/\mid K_{spin} \mid$ without any fitting. As one can see from Fig. 6, the ratio of $(T_1T)^{-1}/\mid K_{spin} \mid$ remains constant even below the spin gap. This result is consistent with the spin dimer theory in which both static and dynamic excitations follow the same temperature variation due to the involvement of a simple singlet-triplet excitation.

III. CONCLUSIONS

In conclusion, we report the first NMR investigation of $Cu_2Sc_2Ge_4O_{13}$ and present evidence for the existence of spin gap in this material. The spin gap of about 275 K deduced from the spin shifts and spin-lattice relaxation rates was found to be identical. A detailed analysis further indicates that the spin gap nature can be well accounted for by the free dimer model. These findings thus allow us to add $Cu_2Sc_2Ge_4O_{13}$ to the family of S =1/2 dimerized spin gap compounds.

ACKNOWLEDGEMENTS

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